Research Highlights

- Hydrothermal synthesis of zeolite N using kaolinite as source of Al and Si
- A range of potassic salts with kaolinite over 100^{o}C to 200^{o}C produces zeolite N
- Limited addition of sodic salts in presence of potassium can produce zeolite N
- Formation conditions at shorter times and lower temperatures than earlier work
- zeolite 4A as source of Al and Si at longer reaction times produces zeolite N

HYDROTHERMAL SYNTHESES OF ZEOLITE N FROM KAOLIN

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Abstract

Zeolite N, an EDI type framework structure with ideal chemical formula $K_{12}Al_{10}Si_{10}O_{40}Cl_2 \cdot 5H_2O$, was produced from kaolin between 100^{o}C and 200^{o}C in a continuously stirred reactor using potassic and potassic+sodic liquors containing a range of anions. Reactions using liquors such as KOH, KOH + KX (where X = F, Cl, Br, I, NO_3, NO_2), K_2X (where X=CO_3), KOH + NaCl or NaOH + KCl were complete (>95% product) in less than two hours depending on the batch composition and temperature of reaction. With KOH and KCl in the reaction mixture and H_2O/Al_2O_3~49, zeolite N was formed over a range of concentrations (1M < [KOH] < 18M) and reaction times (0.5h < t < 60h). At higher temperatures or higher KOH molarity, other potassic phases such as kalsilite or kaliophyllite formed. In general, temperature and KOH molarity defined the extent of zeolite N formation under these conditions. The introduction of sodic reagents to the starting mixture or use of one potassic reagent in the starting mixture reduced the stability field for zeolite N formation. Zeolite N was also formed using zeolite 4A as a source of Al and Si albeit for longer reaction times at a particular temperature when compared with kaolin as the source material.

Keywords: zeolite N; hydrothermal synthesis; kaolin; potassic salts; zeolite 4A

1.0 Introduction

Zeolite N is a potassium-rich aluminosilicate of general formula, $K_{12}Al_{10}Si_{10}O_{40}Cl_2\ 8H_2O$, for which a structural analysis was reported by Christensen and Fjellvag (1997). The synthesis of zeolite N by Christensen and Fjellvag (1997) was based on earlier literature including the seminal study by Barrer et al. (1953). Synthesis of zeolite N was under static hydrothermal conditions at 300^{o}C for a period of 7 days using zeolite 4A and excess potassium chloride in the starting mixture (Christensen and Fjellvag, 1997).

Syntheses of zeolite N, or zeolite K-F(Cl) as described at the time, were given in the work by Barrer et al. (1968), Barrer and Marcilly (1970) and Barrer and Munday (1971). These studies reported that zeolite K-F(Cl) was formed under static hydrothermal conditions at temperatures generally between 200^{o}C and 300^{o}C in the presence of excess KCl over periods of seven days. This early work also interpreted diffraction data for zeolite K-F(Cl) as a tetrahedral structure. The structure determinations by Christensen and Fjellvag (1997; 1999) using high resolution X-ray and neutron diffraction data, showed that zeolite N is orthorhombic with space group I222.

More recently, manufacture of zeolite N at low temperatures (<100^{o}C) using kaolinite and montmorillonite as starting materials was reported by Mackinnon et al. (2010). General conditions for production of zeolite N in a continuously stirred reactor were reported for $60^{o}C < T < 100^{o}C$ and included combinations of potassic and sodic caustics and/or salts in the starting mixture. These conditions for synthesis of zeolite N (Mackinnon et al., 2010) were at lower temperature and for shorter times than previously reported by Christensen and Fjellvag (1997).

Zeolite N has been identified as a viable material for selective ion exchange applications, in particular for the exchange of ammonium ion in aqueous solution (Thornton et al.

2007a, b; Mackinnon et al. 2003) and for use in the treatment of sandy soils (Zwingmann et al., 2009). More recently, Zwingmann et al. (2011) have noted the potential anti-fungal properties of this material when used as a soil amendment for delivery of N and/or K to crops. This work presents new data on the hydrothermal synthesis of zeolite N and extends the range of potassic salts used in the starting mixture.

2.0 Experimental

A sealed stainless steel, thermocouple controlled reactor was used for all syntheses reported in this study. The volume of reactor was approximately 1 L. The reactor was configured for continuous stirring of the reaction mixture. Synthesis procedures involved the dissolution of potassium and/or sodium reagents in water, stirring and heating the reaction liquor to $95^{o}C < T < 100^{o}C$. The required amount of aluminosilicate was added to the reaction mix with constant stirring, and once the reactor was sealed, rapidly increased to the specified reaction temperature. Nominal pressure within the reactor during this process ranged from 2bar to 4bar. The reaction was stopped by reducing the temperature to less than $60^{o}C$ by adding room temperature water to the reactor. Solid product was removed from the mother liquor by filtration or sedimentation in a separate wash tank. All products were water washed until the reject stream showed pH < 10.5. The washed slurry product was then oven dried at $105^{o}C$ to obtain the powder.

A typical reaction sequence for the production of zeolite N with potassium-based reagents used a 1L stainless steel Teflon-lined reactor tank filled with 221mL of water supplied by a conventional domestic reticulated system. To this solution, 66g of 98% solid potassium hydroxide and 66g of 98% solid potassium chloride were slowly added. This caustic solution was stirred and heated to $95^{o}C$. While the solution was at this temperature, 66g of kaolin was added to the reaction mix while stirring (this ratio of reagents was equivalent to

reaction 1, Table 1). At this point, the reactor was sealed and rapidly increased to the specified temperature of reaction.

Based on earlier work (Mackinnon et al., 2010), the pH of this reaction mix was generally greater than 14.0 and during the course of the reaction reduced to approximately 13.5. During the reaction process – approximately 0.25 hour to 0.50 hour after the kaolin was added to the reactor – the viscosity of the mixture increased. After mixing at temperatures >100^{o}C ± 5^{o}C, the reaction was stopped by reducing the temperature to less than 50^{o}C *via* addition of water, rapidly removing the product from the reactor or both methods. The weight of dried zeolite N from this reaction was approximately 87g. This amount of product gave a yield greater than 90% for the reaction shown below:

$$5Al_2Si_2O_5(OH)_4 + 10KOH + 2KCl + H_2O \rightarrow K_{12}Al_{10}Si_{10}O_{40}Cl_2 \cdot 8H_2O + 8H_2O \quad (1)$$

A range of aluminosilicate starting materials have been used in hydrothermal experiments and have been detailed in earlier publications (Mackinnon et al., 2006, 2010). Syntheses reported in this study used kaolin (Kingwhite 65) from Kingaroy Kaolin Pty Ltd. Physical and chemical properties of this kaolin are given in Table 1. Potassium and sodium starting materials were industrial grade KCl (Redox Chemicals, POCHLO16), KOH (Redox Chemicals, caustic potash Capota45), NaCl (Cheetham Salt, Superfine grade) and NaOH (Redox Chemicals). Sodic zeolite 4A used for comparative reactions was supplied by PQ Corporation. Solutions were made with potable water from the local reticulated supply. Other salts such as KF, KBr, KI, K_2CO_3, KNO_3 and KNO_2 were AR grade provided by Selby Scientific Pty Ltd.

X-ray data were collected on a Bruker automated powder diffractometer using CuKα radiation (λ=1.5406) between 2^{o} and 70^{o} 2θ at a scan speed of 1^{o} 2θ per minute with a 2θ step of 0.02^{o} using quartz as a calibration standard. All intensities in XRD patterns in this paper have been normalized to I_{max} = 100 counts. Cell dimensions and indices for zeolite N

samples were obtained by least-squares refinement from X-ray powder diffraction patterns using the data determined by Christensen and Fjellvag (1997). Least-squares refinements on cell dimensions used a two-theta tolerance of ±0.1^{o} (*i.e*. difference between observed and calculated reflections) for convergence. Cation exchange capacities (CECs) were determined experimentally for equilibrium exchange of ammonium ion in a 1M NH_4Cl solution as described earlier (Mackinnon et al., 2010) calibrated against the method of Jaynes and Bingham (1986). CEC values for the materials in this work were determined on a "wet mass" basis.

3.0 Results

More than 150 hydrothermal reactions, including repeat syntheses, have been undertaken using kaolin as a starting aluminosilicate. In earlier work Mackinnon et al. (2010) demonstrated that the extent of transformation to zeolite N under the same reaction conditions depended on the type of kaolin used. In this study, we have compiled data for reactions using only Kingwhite 65 kaolin or zeolite 4A from PQ Corporation.

Examples of synthesis conditions from a range of starting compositions as molar ratios relative to Al_2O_3 (*e.g.* K_2O/Al_2O_3) are listed in Tables 2–5. These starting compositions show a range of products, temperatures and reaction times used to evaluate the extent of zeolite N formation. For these reactions, powder XRD was used to identify phases in the final product. A number of reaction conditions resulted in production of zeolite N as shown in these tables. In general, XRD patterns showed the presence of one major phase albeit with minor or trace levels of impurity phases such as quartz.

Fig. 1 shows a series of XRD patterns for the starting composition of reaction 1 (Table 2) at various temperatures for two hours. At 110^{o}C, the XRD pattern showed that precursor KAD phase (Mackinnon et al., 2010) was dominant with un-reacted kaolin (reflections

123 marked “K”) and minor amounts of zeolite N (reflections marked “N”) present. As shown
124 in Mackinnon et al. (2010), KAD is an amorphous phase formed from kaolin by caustic
125 reaction with potassic salts and is an intermediate, or precursor, phase that can lead to the
126 formation of zeolite N. The XRD pattern for KAD, an acronym for “kaolin amorphous
127 derivative” (Thompson et al., 1999), is characterized by the presence of a significant
128 “amorphous” hump with high background for ~$25^{o} < 2\theta < 35^{o}$. At higher temperature,
129 between 130°C and 175°C, the XRD pattern for zeolite N was well-defined with no other
130 phases present. At temperatures above 200°C, kalsilite formed as shown in Fig. 1.
131 Experimentally determined CEC values for the respective phases were consistent with the
132 XRD data.

133 Fig. 2 shows XRD patterns for reactions with a constant KCl concentration and increasing
134 KOH concentration in the starting composition. The parameters for reactions 3–6 are listed
135 in Table 2 and show that for [KOH] < 16.0M the primary product was zeolite N with
136 kaliophyllite dominant at higher KOH concentrations. Fig. 3 shows XRD patterns for
137 reaction conditions with KOH and KCl in which the ratio of H_2O/Al_2O_3 was varied by a
138 factor of five (reactions 4 and 12). Zeolite N formed across a broad range of H_2O/Al_2O_3
139 values for T=130°C and reaction time of two hours in the presence of KCl. In these cases,
140 the product was zeolite N with high values of CEC.
141 Table 2 also lists products obtained from reaction of kaolin and KOH at different
142 concentrations in the absence of KCl (reactions 7–10). Fig. 4 shows XRD patterns for a
143 starting composition of reaction 7 (Table 2) in which KOH molarity was varied. Fig. 4
144 shows that in the absence of KCl, kaliophyllite formed when the molarity of KOH was
145 greater than 16.0 and at lower KOH molarity ([KOH] ≤ 5.3M), the precursor KAD phase
146 was predominant. The temperature and time of reaction were the same for these reactions.

147 Table 2 also shows a range of other parameters (reactions 11, 14, 15) that, among others,
148 defined the extent of conditions under which zeolite N occurred in the final product.

149 Table 3 provides a range of experimental conditions in which the potassic salt, KX where
150 X=Br, I or F ion, is added to the reaction mix with [KOH] = 5.3M. Fig. 5 shows XRD
151 patterns for reactions 21–23 in Table 3 compared with the previous syntheses using KCl
152 (equivalent composition to reaction 1, Table 2 but with different time and temperature of
153 reaction). In these syntheses, the ratio K_2O/Al_2O_3 = 2.3 and the temperature of reaction
154 was 130^{o}C for four hours. In all cases, XRD patterns showed that zeolite N was the
155 predominant phase. Minor amounts of impurities and/or quartz were present in the final
156 product.

157 Table 3 also lists examples of hydrothermal reactions using other potassic salts such as
158 K_2CO_3 and KNO_2.over a range of temperature and time conditions (reactions 24–29). Fig.
159 6 shows XRD patterns for products of these syntheses compared with the synthesis using
160 KCl (equivalent to reaction 1, Table 2 but for two hours and at 130^{o}C). Note that for
161 shorter reaction times, an increase in the background signal for XRD patterns between 25^o
162 $< 2\theta < 40^o$ was consistent with the presence of minor amounts of precursor KAD material
163 (Mackinnon et al., 2010). The dominant phase for many of these reactions was zeolite N
164 with minor amounts of quartz (Fig. 6).

165 Table 4 lists typical starting compositions using sodic reagents at 130^{o}C for two hours.
166 Reactions 30–33 resulted in production of zeolite N while reaction 32, with a higher
167 sodium content, resulted in formation of sodalite. For reaction 29, minor amounts of leucite
168 were also present in the final product under these conditions (data not shown).

169 Table 5 lists reaction conditions for syntheses using zeolite 4A as the aluminosilicate
170 source. Reactions 34–39 were undertaken at 130^{o}C for times ranging from two hours to 64

hours and additions of either KOH or KCl or both potassic reagents. For many reactions, un-reacted zeolite 4A and sodalite were the primary products. However, zeolite N was formed at this temperature at longer reaction times (> 60 hours). Reactions 40 and 41 were at higher temperature (175^{o}C) and resulted in formation of zeolite N. Reaction 42 was undertaken at conditions similar to that described by Christensen and Fjellvag (1997) except that the reactor was continuously stirred during the process.

4.0 Discussion

Mackinnon et al. (2010) outlined the range of studies previously undertaken in the synthesis of potassic zeolites, and in particular, focused on the limited number of syntheses under ambient conditions at reaction temperatures <100^{o}C. This study utilizes the starting compositions identified in Mackinnon et al (2010) to explore the stability of zeolite N under a wide range of hydrothermal reaction conditions. In both of these studies, differences in approach compared with early syntheses in potassic aluminosilicates included larger sample sizes (many grams compared with milligrams) and analytical techniques (e.g. early syntheses relied on film-based X-ray techniques from small amounts of sample).

For the temperature range considered in this study, early work by Barrer and colleagues suggested that products of hydrothermal reaction with potassic reagents between 100^{o}C and 200^{o}C for reaction times between two days and ten days, were zeolite K-F (Barrer and Marcilly, 1970), kaliophyllite (Barrer and Marcilly, 1970; Barrer et al., 1968) or chabazite (Barrer et al., 1968). Data presented in this work show that zeolite N, or as previously known zeolite K-F(Cl), may also form *via* hydrothermal reaction with potassic reagents between 100^{o}C and 200^{o}C.

4.1 KOH ± KCl reactions with kaolin

In this work, zeolite N was formed over time periods of a few hours at temperatures between 100°C and 200°C in a stirred reactor. In these hydrothermal reactions, kaolin and potassic salts were critical ingredients for the production of zeolite N. For a given type of reaction, systematic variation of reaction temperature allowed an estimate of the maximum and minimum temperatures at which zeolite N formed.

As demonstrated by Christensen and Fjellvag (1997) and Mackinnon et al. (2010), facile production of zeolite N was effected with excess amounts (i.e. non-stoichiometric) of KCl in the reactor. These conditions allowed production of zeolite N under static hydrothermal conditions (Christensen and Fjellvag, 1997) and under continuously stirred low temperature conditions (Mackinnon et al., 2010) with KOH present. Under the dynamic hydrothermal conditions of this study, the temperatures at which zeolite N formed were clearly different to previous work.

For example, XRD data (summarized in Fig. 1) showed that for H_2O/Al_2O_3 ~49, the predominant phase at 175°C was zeolite N when reacted for two hours. The formation of kalsilite was detectable at temperatures above 200°C when reacted for more than two hours (reaction 16, Table 2). Under hydrothermal conditions, the formation of the intermediate KAD phase occurs in less time (< 2hrs) at higher temperature (reactions 19 and 20 Table 2; Fig. 1) compared with the conditions described by Mackinnon et al. (2010). High concentrations of KOH in the starting mixture drove the reaction toward formation of other phases such as kaliophyllite (reactions 6 and 13, Table 2) unless an excess amount of KCl was added to the mixture (reaction 12, Table 2).

Fig. 2 shows that for reaction times of two hours at 130°C, zeolite N formed over a wide KOH concentration range – from < 5.3M to >16.0M – in the presence of excess KCl. With additional reaction time, CEC values of zeolite N increased for a given temperature of reaction. For example, for the reactant ratios of reaction 18 (Table 2), the CEC value

increased from 479 to 500meq/100g when the reaction time was increased from 2 hours to 6 hours. However, as shown in Fig. 4, in the absence of KCl, zeolite N formed over a lower KOH concentration range between 10.7M and less than 16.0M at the same temperature. This dependence on [KOH] is also shown by the sequence of reactions 7–10 in Table 2. This lower range of stability of zeolite N in reactions without KCl was also noted for lower temperature synthesis (Mackinnon et al., 2010).

As identified by Mackinnon et al. (2010) for low temperature reactions, the robustness of the synthesis process was optimum with both KOH and KCl in the reaction mixture. Similarly, under hydrothermal conditions, within a broad range of KOH and KCl molarity, temperature ($100^{o}C < T < 200^{o}C$) and time (1 hour < t < 60 hours), zeolite N was obtained. For the conditions shown as reaction 1 in Table 2, the average CEC value for 46 replicate syntheses was 502 meq/100g with a calculated standard deviation of 8 meq/100g.

At temperatures below $130^{o}C$, the formation of zeolite N required a longer reaction time. For example, Fig. 1 shows a dominant KAD phase with minor presence of zeolite N after two hours reaction at $110^{o}C$ (reaction 20). At four hours reaction time at $110^{o}C$, (00*l*) reflections for zeolite N were more apparent (XRD data not shown) while KAD (Mackinnon et al., 2010) was less apparent.

In addition, the KOH + KCl reaction with KCl in excess, was independent of water content for the range of values $48 < H_2O/Al_2O_3 < 485$. Fig. 3 shows XRD traces for two zeolite N products from reactions 12 and equivalent to reaction 4 at two different ratios of H_2O/Al_2O_3. For reference, key reflections for the zeolite N structure are indexed in Fig. 3. For the KOH + KCl suite of reaction conditions, formation of zeolite N is less dependent on the level of water (*i.e.* solids content) than the level of caustic present in the reaction mixture.

4.2 KOH ± KX (X≠ Cl) or KOH ± NaX reactions with kaolin

The reactions with KOH and KCl suggested that under hydrothermal conditions with constant mixing, varieties of zeolite N may be formed using different potassic salts. The products of reaction using different potassic salts are shown in Figs. 5 and 6 and are compared with the equivalent KOH + KCl reaction under the same temperature and time conditions. For similar concentrations of potassic salts such as KF, KI and KBr (Fig. 5) and KNO_3, $KN0_2$ and K_2CO_3 (Fig. 6), zeolite N was formed. Table 3 lists the parameters for these reactions. Reactions 25 and 29 indicated that there was a limit to the temperature at which zeolite N formed with these other potassium salts.

Refined cell dimensions for these different varieties of zeolite N formed with potassic salts and KOH are shown in Table 6. Cell dimensions for the *c*-axis of zeolite N produced with different potassium salts showed an expected strong correlation ($r^2 = 0.98$) with the type of anion in the structure. This correlation of cell dimensions with anion type is consistent with the structure determination of the type zeolite by Christansen and Fjelvag (1997) which showed that Cl^- ions are coordinated with six K^+ ions in a distorted octahedral arrangement. These non-framework atoms, as ClK_6 octahedra, fill voids in the channels running along [001] (Christensen and Fjelvag, 1997). In this zeolite N structure, potassium atoms are bonded to both framework (Al, Si) and non-framework atoms (Cl, O). Similarly, we propose that zeolite N formed by reaction with other potassic salts will contain void-filling distorted octahedral arrangements such as IK_6 and BrK_6.

Barrer and Marcilly (1970) identified two other crystalline aluminosilicates of tetrahedral structure that formed at temperatures above 200^{o}C. These structures – termed zeolite K-F(Br) and zeolite K-F(I) – were formed at 240^{o}C and 320^{o}C, respectively, over periods of four days. Zeolite K-F(Br) was also referred to as zeolite O (Barrer and Marcilly, 1970). This study suggests that, as with the Cl form of zeolite N, the Br and I forms of zeolite N

may be synthesized at temperatures lower than 200^{o}C and that both may form an octahedral, rather than tetrahedral, structure.

Hydrothermal syntheses with sodic reagents for selected reactions are shown in Table 4. These reactions showed that NaCl may be used to replace KCl in the hydrothermal synthesis of zeolite N as demonstrated at low temperature (Mackinnon et al., 2010) with continuous mixing. Similarly, modest amounts of NaOH in the initial reaction mixture also resulted in formation of zeolite N provided both KOH and KCl were present. Other reactions showed that increased addition of sodium to the reaction mixture resulted in formation of sodalite. For example, with reaction 33 (Table 4) the concentration of NaOH is significantly higher than KOH but even with excess KCl, the final product after two hours reaction at 130^{o}C was sodalite.

4.3 KOH ± KCl reactions with zeolite 4A

Christensen and Fjellvag (1997) prepared zeolite N by a static hydrothermal reaction using zeolite 4A as the starting material. Accordingly, a number of experiments were undertaken over extended periods of time with zeolite 4A instead of kaolin. Selected data from these experiments are given in Table 5. These data show that at 130^{o}C, longer reaction times (> 15 hours) are required to effect formation of zeolite N with continuous stirring of the reaction mixture provided the reagent concentrations are similar to that for successful production of zeolite N from kaolin.

The CEC value for zeolite N formed at 130^{o}C from zeolite 4A (reaction 36, Table 5) is significantly lower than commonly obtained with kaolin as the starting material at shorter reaction times. Lower values of CEC for zeolite N formed from zeolite 4A also occurred for reactions at higher temperature (e.g. reaction 40). However, with zeolite 4A and only KOH in the starting mixture, reactions for longer times or higher temperature showed higher CEC values (e.g. reactions 39 and 41) and XRD patterns consistent with zeolite N.

Mackinnon et al. (2010) suggested that a CEC value >400meq/100g was a good indicator for the presence of zeolite N when using kaolin as source material. However, this does not apply when zeolite 4A was used as source material because un-reacted zeolite 4A also has a high CEC value (e.g. reactions 34, 35, 37 and 38). The CEC value measured for zeolite 4A used in this study was 492±6 meq/100g.

Fig. 7 compares the XRD data for products from reaction with kaolin (reaction 2, Table 2) and two products from reaction with zeolite 4A (reactions 36 and 41). All traces showed typical reflections for zeolite N although products of reaction with zeolite 4A showed significantly sharper reflection profiles and lower backgrounds compared with XRD traces for kaolin-derived products. The anomalous CEC value for zeolite N in reaction 36 (and, by implication, reaction 40) may be explained by close inspection of XRD patterns for reactions 36 and 41(Fig. 7). These patterns show that the product with higher CEC value showed significantly enhanced primary reflections (e.g. (220) and (004)), lower background and relative peak ratios for (222), (114) and (132) that were commonly encountered when a zeolite N reaction has gone to completion (e.g. compare with Fig. 3 and data in Mackinnon et al., 2010). Differences in peak heights as well as the higher background XRD signal for the product of reaction 36 suggest that at 130^{o}C the transformation to zeolite N is sluggish (compared with using kaolin as starting material) and that dissolution of starting materials is complete. Based on earlier work, the higher background in XRD patterns for kaolin-derived zeolite N indicated the presence of an intermediate amorphous phase termed KAD (Mackinnon et al., 2010). For reaction 36, an intermediate amorphous phase may also be present and re-growth of zeolite N crystals may not be fully completed after reaction for 17 hours at 130^{o}C. Detailed examination by other techniques may be necessary to establish whether an intermediate phase occurred in the formation of zeolite N from zeolite 4A by these reactions.

Similarly, reaction 40 in Table 4 showed that zeolite 4A when reacted with a higher chloride content (compared with reaction 41) formed zeolite N with a low CEC value of 225meq/100g. Both reactions 40 and 41 were for 2 hours at 175^{o}C. The XRD pattern for reaction 40 (data not shown) showed similar characteristics to that described above for reaction 36. Thus, it is likely that for lower temperature reactions or for reactions with lower KOH concentration, formation of zeolite N was less favourable. The impact of potassium chloride on formation of zeolite N when using zeolite 4A is supported by all reaction data in Table 5. These data suggest that formation of zeolite N from zeolite 4A in the presence of excess chloride salt was not favoured compared with reaction with KOH only.

4.4 Time–temperature relationships

A compilation of data points for the KOH + KCl reaction over a range of reaction times and temperatures is shown in Fig. 8. This time-temperature-transformation plot incorporates data presented in earlier work for the synthesis of zeolite N at T < 100^{o}C (Mackinnon et al., 2010). For a specific reaction mixture condition (e.g. K_2O/Al_2O_3, H_2O/Al_2O_3 and KCl/Al_2O_3 equivalent to reactions 1, 15 and 16 in Table 1), zeolite N formed over a wide range of temperatures, from > 60^{o}C to 200^{o}C, and times, ranging from 30 minutes to > 60 hours. This stability field is significantly larger than that identified by Barrer and colleagues and, more recently, by Christensen and Fjellvag (1997) under static hydrothermal conditions (shown schematically in Fig. 8).

Molarity data from KOH + KCl reactions including data from Mackinnon et al. (2010) are shown in Fig. 9. In this plot of KOH molarity against reaction temperature, zeolite N formed over a wide range of KOH concentrations – from <1.0M to >18.0M. These reactions occurred over a range of time periods and, as shown in Fig. 9, many produced zeolite N. The region explored by Barrer et al. (1968), Barrer and Marcilly (1970) and

Barrer and Munday (1971) under static hydrothermal conditions is also shown on Fig. 9. This plot shows that the conditions for zeolite N formation have been extended beyond those initially identified for zeolite K-F(Cl) by Barrer et al. (1968) and colleagues.

5.0 Conclusions

Hydrothermal synthesis of zeolite N was demonstrated for the temperature range $100^{o}C < T < 200^{o}C$ for a range of initial batch compositions using kaolin as the source of Al and Si. Depending on the temperature of reaction, these syntheses produced zeolite N over times ranging from < 1hour to ~ 60 hours. Data from low temperature ambient pressure syntheses (Mackinnon et al., 2010) and this study have shown that an initial batch composition with both KCl and KOH at similar molar concentrations and $H_2O/Al_2O_3 \sim 50$ produced zeolite N over a broad time-temperature range from $60^{o}C < T < 200^{o}C$ and 0.5 hour < t < 120 hours.

At higher temperatures or higher KOH molarity, other potassic phases such as kalsilite or kaliophyllite formed. Incomplete, or lower temperature, reaction for these syntheses with kaolin produced the intermediate material KAD (Mackinnon et al., 2010). The time-temperature-transformation field was more limited for other initial batch compositions including partial replacement of KCl or KOH with NaCl and NaOH, respectively. For reactions using sodium in the starting mixture, production of zeolite N was dependent on the molar concentration of NaOH in the reaction.

Hydrothermal syntheses using other potassic salts (such as KX, where X=F, I, Br, NO_2 or NO_3) under similar initial batch compositions produced zeolite N at relatively short reaction times (< 4 hours). At higher water contents ($H_2O/Al_2O_3 \sim 96$), zeolite N was also formed from zeolite 4A using either KOH or KOH+KCl in the starting mixture at $130^{o}C < T < 175^{o}C$. Reactions with zeolite 4A at higher temperature, longer times and higher water

content, similar to the static hydrothermal reaction described by Christensen and Fjellvag (1997) produced kalsilite. This study demonstrated production of zeolite N under significantly different conditions to earlier studies that reported production of zeolite K-F(Cl) or zeolite N at higher temperatures (> 200^{o}C) and longer times (> 150 hours) in a closed, static reactor.

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Figure Captions

Fig. 1. Powder XRD patterns for two hour hydrothermal synthesis with kaolin at different reaction temperature using an initial reaction mixture (reaction 1 or 18, Table 2) showed three different products: KAD, zeolite N or kalsilite. Unreacted kaolin (reflections designated “K”) and zeolite N (reflections designated “N”) were also present at low temperature of reaction.

Fig. 2. Powder XRD patterns for two hour hydrothermal synthesis with kaolin at different KOH concentrations and constant KCl concentration in the initial reaction mixture produced zeolite N (reactions 3–5) or kaliophyllite (reaction 6).

Fig. 3. Powder XRD patterns for two hour hydrothermal synthesis with kaolin at different water contents in the initial reaction mixture produced zeolite N. Indexed reflections for zeolite N are in parentheses.

Fig. 4. Powder XRD patterns for two hour hydrothermal synthesis with kaolin at different KOH concentrations and no KCl in the initial reaction mixture produced KAD, zeolite N or kaliophyllite (reactions 7–10, Table 2).

Fig. 5. Powder XRD patterns for four hour hydrothermal synthesis with kaolin and different potassium salts in the initial reaction mixture produced zeolite N (reactions 21–23, Table 2).

441 Fig. 6. Powder XRD patterns for two hour hydrothermal synthesis with kaolin and
442 different potassium salts in the initial reaction mixture produced zeolite N (reactions 18,
443 24, 26, 27; Table 2).

444

445 Fig. 7. Powder XRD patterns for hydrothermal synthesis with zeolite 4A (reactions 36 and
446 41) and with kaolin (reaction 2) produced zeolite N. Reactions 2 and 41 resulted from
447 synthesis at 175^{o}C for two hours. Indexed reflections for zeolite N are in parentheses.

448

449 Fig. 8. Plot of phases produced with syntheses from Kingwhite 60 kaolin using the same
450 initial reaction mixture over a range of temperatures and times of reaction. For comparison,
451 the approximate locations of earlier syntheses of zeolite N, also reported as zeolite K-
452 F(Cl), are shown (hatched area).

453

454 Fig. 9. Plot of phases produced with syntheses from kaolin over a range of initial KOH
455 concentrations and temperatures of reaction. For comparison, the approximate locations of
456 earlier syntheses of zeolite N are shown (hatched area).

Table 1

Properties of kaolin starting material KW65 for zeolite N syntheses

Chemical Analysis (wt % oxide)	**Kingwhite 65**
SiO_2	47.10
Al_2O_3	36.69
FeO	1.19
CaO	0.10
MgO	0.14
Na_2O	0.09
K_2O	0.17
TiO_2	0.99
LOI	13.52
Si/Al ratio	1.09
CEC (meq/100g)	12
Particle size (μm) d_{50}	8.3
d_{10}	2.3
d_{90}	21.0
% kaolinite by XRD	99*
% quartz by XRD	trace*
Surface area (m^2/g)	16*
pH (in 20% slurry)	6.8*
ISO Brightness	84*

*Values from supplier specification sheet

Table
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Table 2

Reaction parameters – potassium reagents with kaolin

Reaction	**K_2O/Al_2O_3**	**KCl/Al_2O_3**	**H_2O/Al_2O_3**	**Temp** (^oC)	**Time** (hours)	**CEC** (meq/100g)	**Primary Product**
1	2.3	3.5	48.5	175	2	517	zeolite N
2	1.2	3.5	48.3	175	2	482	zeolite N
3	2.3	1.7	48.5	130	2	462	zeolite N
4	4.6	1.7	49.0	130	2	504	zeolite N
5	6.9	1.7	49.5	130	2	410	zeolite N
6	9.2	1.7	50.0	130	2	150	kaliophyllite
7	2.3	0.0	48.5	130	2	387	KAD
8	4.6	0.0	49.2	130	2	495	zeolite N
9	6.9	0.0	49.5	130	2	225	ZN+kalioph
10	9.2	0.0	50.0	130	2	104	kaliophyllite
11	4.6	6.9	97.0	130	2	508	zeolite N
12	11.5	17.3	242.6	130	2	509	zeolite N
13	11.5	1.7	49.5	130	2	139	kaliophyllite
14	2.3	3.5	48.5	150	63	514	zeolite N
15	2.3	3.5	48.5	175	18	514	zeolite N
16	2.3	3.5	48.5	250	2	13	kalsilite
17	2.3	3.5	96.5	130	2	285	kaolin+KAD
18	2.3	3.5	48.5	130	2	479	zeolite N
19	1.2	5.8	24.3	130	2	321	KAD+kaolin
20	2.3	3.5	48.5	110	2	380	KAD+ZN

Table 3

Reaction parameters and products – other potassium salts with kaolin

(for [KOH]=5.3M; [KX]=3.5M; H_2O/Al_2O_3=48.5)

Reaction	**Salt**	**Temp** (^oC)	**Time (hours)**	**CEC** (meq/100g)	**Primary Product**
21	KI	130	4	452	zeolite N
22	KBr	130	4	486	zeolite N
23	KF	130	4	468	zeolite N
24	K_2CO_3	130	2	446	zeolite N
25	K_2CO_3	175	2	33	kalsilite
26	KNO_2	130	2	438	zeolite N
27	KNO_3	150	2	472	zeolite N
28	KNO_2	175	2	385	zeolite N
29	KNO_2	200	17	25	kaliophylite

Table 4

Reaction Parameters – Potassium and Sodium Reagents with kaolin

(at T=130^{o}C for 2 hours)

Reaction	**K_2O/Al_2O_3**	**KCl/Al_2O_3**	**H_2O/Al_2O_3**	**Na_2O/Al_2O_3**	**$NaCl/Al_2O_3$**	**CEC** (meq/100g)	**Primary Product**
30	2.3	0.0	48.5	0.0	1.0	471	zeolite N
31	1.7	3.5	49.5	1.1	0.0	503	zeolite N
32	2.3	0.0	48.5	0.0	0.4	446	zeolite N
33	0.7	4.2	51.4	3.2	0.0	255	sodalite

Table
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Table 5

Reaction Parameters – potassium reagents with Zeolite 4A

(Na_2O/Al_2O_3 = 1.0)

Reaction	**K_2O/Al_2O_3**	**KCl/Al_2O_3**	**H_2O/Al_2O_3**	**Temp** (^oC)	**Time** (hours)	**CEC** (meq/100g)	**Primary Product**
34	3.3	4.9	96.0	130	2	470	4A+Sodalite
35	3.3	4.9	96.0	130	6	419	4A+Sodalite
36	3.3	4.9	96.0	130	17	251	zeolite N
37	0.0	4.9	95.0	130	16	464	4A+Sodalite
38	3.3	0.0	96.0	130	16	483	4A+Sodalite
39	3.3	0.0	96.0	130	64	357	zeolite N
40	3.3	4.9	96.0	175	2	225	zeolite N
41	6.5	0.0	96.7	175	2	464	zeolite N
42	0.0	12.3	231.0	300	170	3	kalsilite

Table
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Table 6

Refined cell dimensions for zeolite N produced from a range of starting materials

Reaction No.	**a** (pm)	**b** (pm)	**c** (pm)	**Cell Volume** ($x10^6$ pm^3)
Reaction 1	991.4(2)	987.6(2)	1307.1(3)	1279.8
Reaction 3	994.5(2)	986.0(2)	1306.2(3)	1280.8
Reaction 8	992.3(2)	983.7(2)	1309.7(3)	1278.5
Reaction 11	994.0(2)	984.9(2)	1310.2(3)	1282.6
Reaction 12	995.4(2)	984.4(2)	1312.5(3)	1286.1
Reaction 31	993.7(2)	985.4(2)	1312.3(3)	1285.0
Reaction 23	993.8(2)	984.7(2)	1306.1(3)	1278.2
Reaction 22	993.9(3)	986.3(3)	1311.5(4)	1285.7
Reaction 21	994.7(2)	983.7(2)	1312.2(3)	1284.0
Reaction 27	995.1(2)	986.1(2)	1307.9(3)	1283.4
Reaction 26	993.6(2)	985.7(2)	1308.2(3)	1281.2
Reaction 24	992.4(2)	985.0(2)	1310.1(3)	1280.8

Figure

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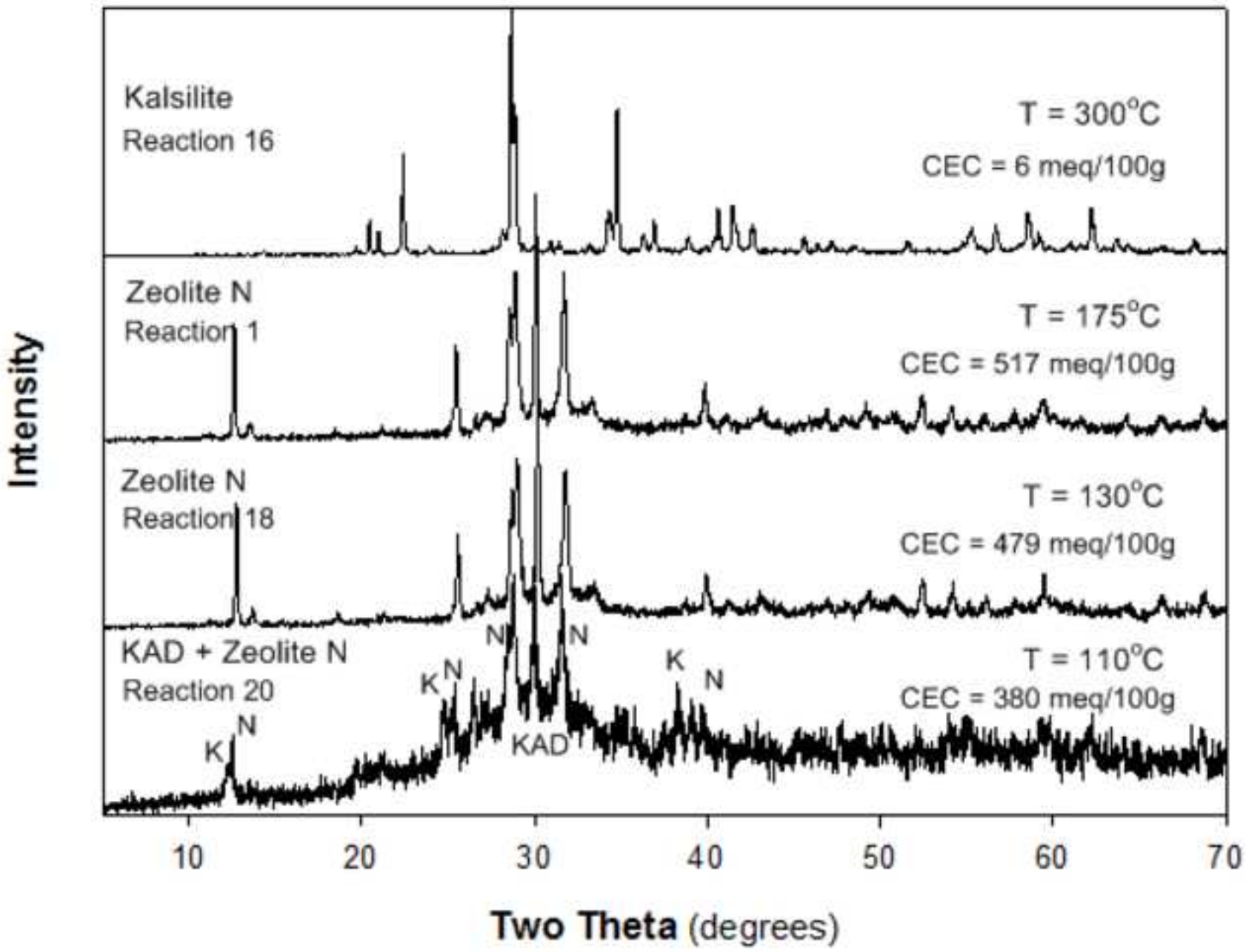

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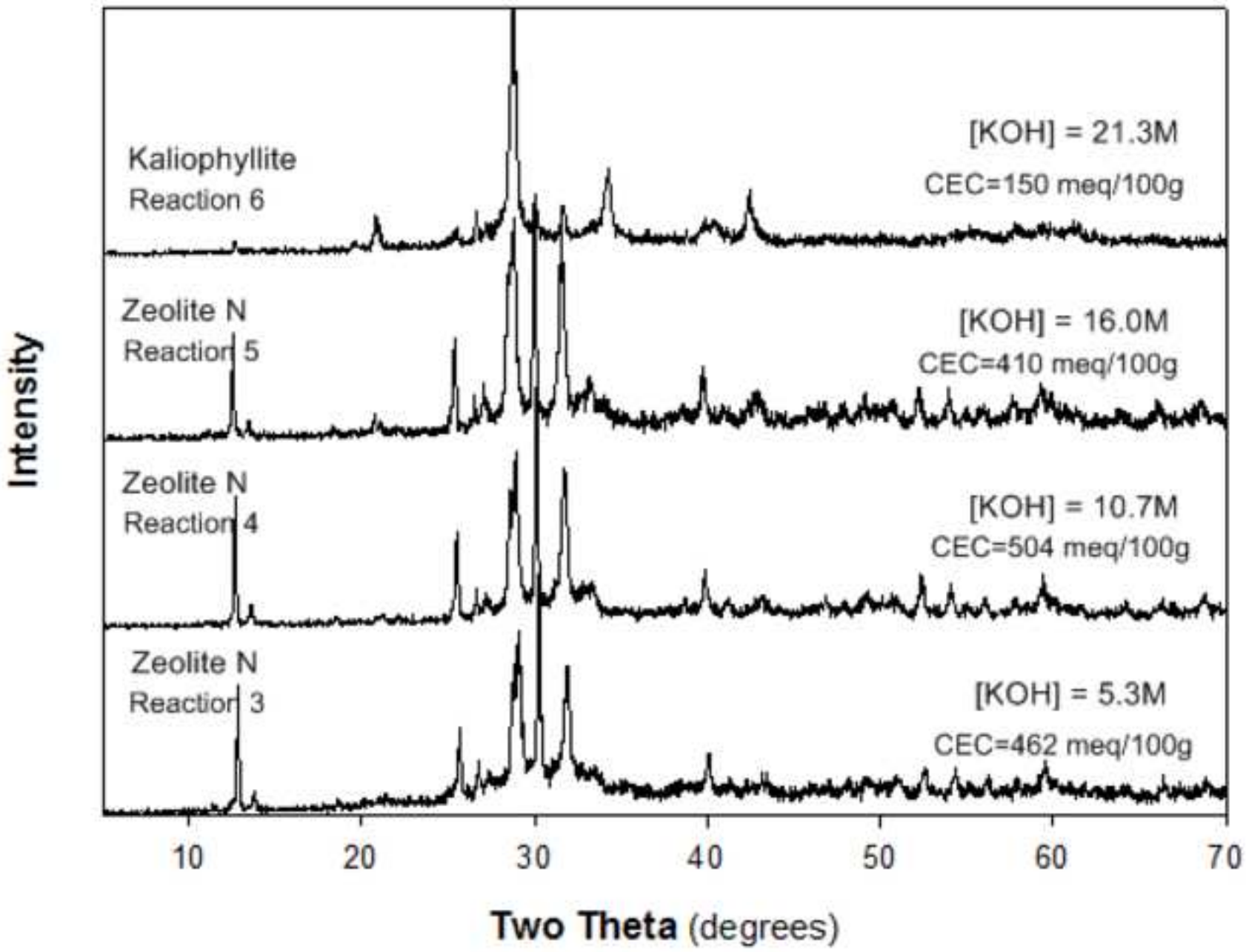

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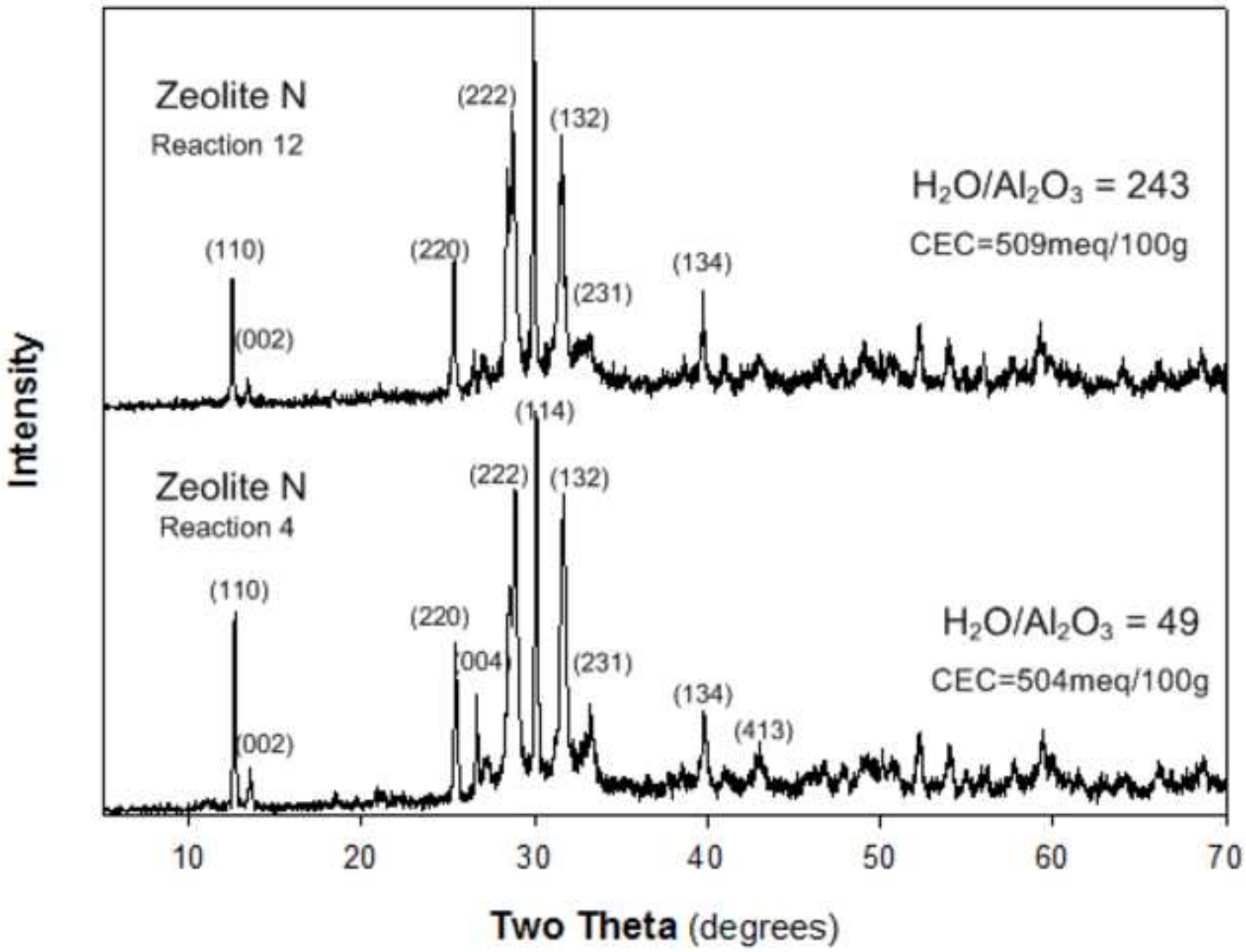

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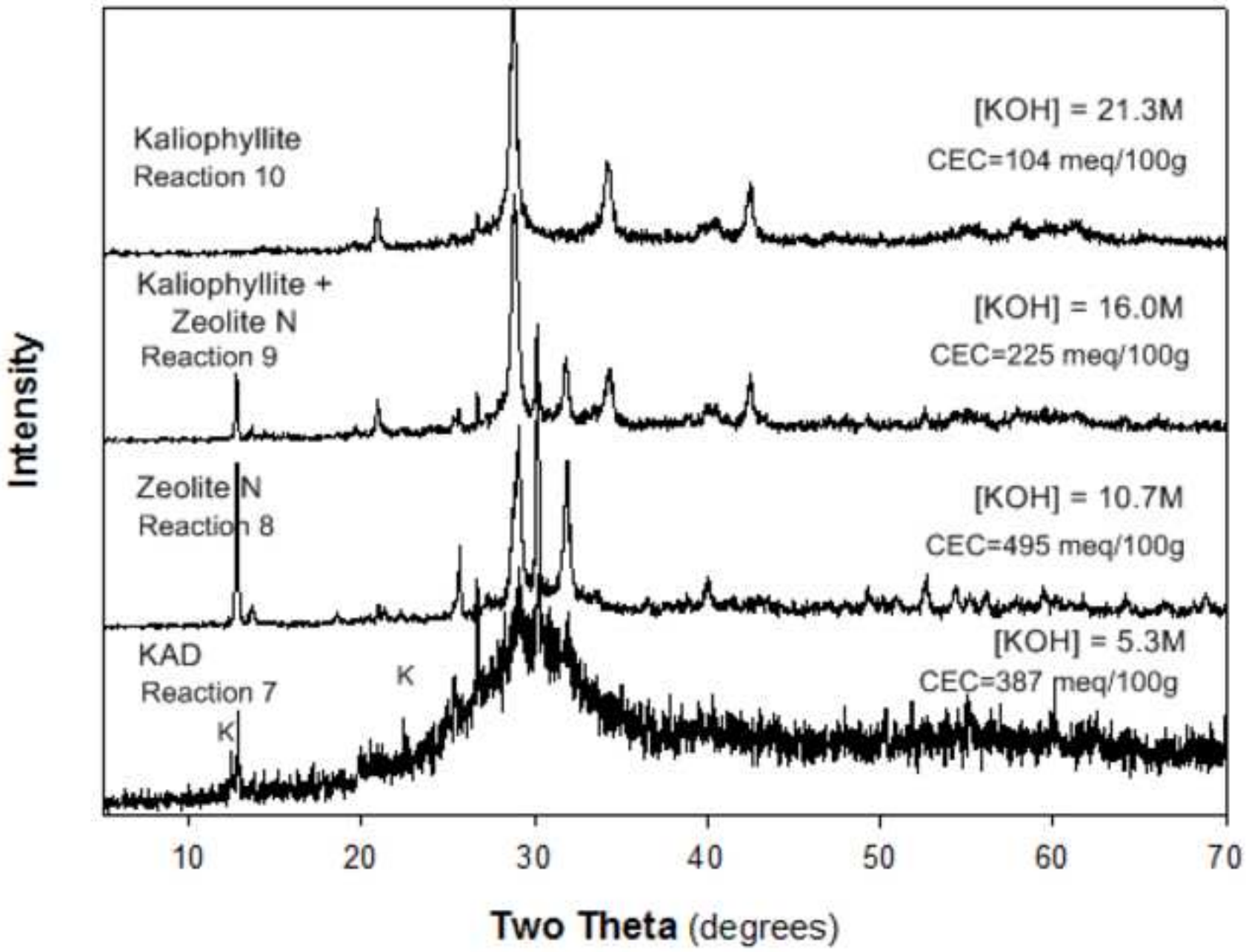

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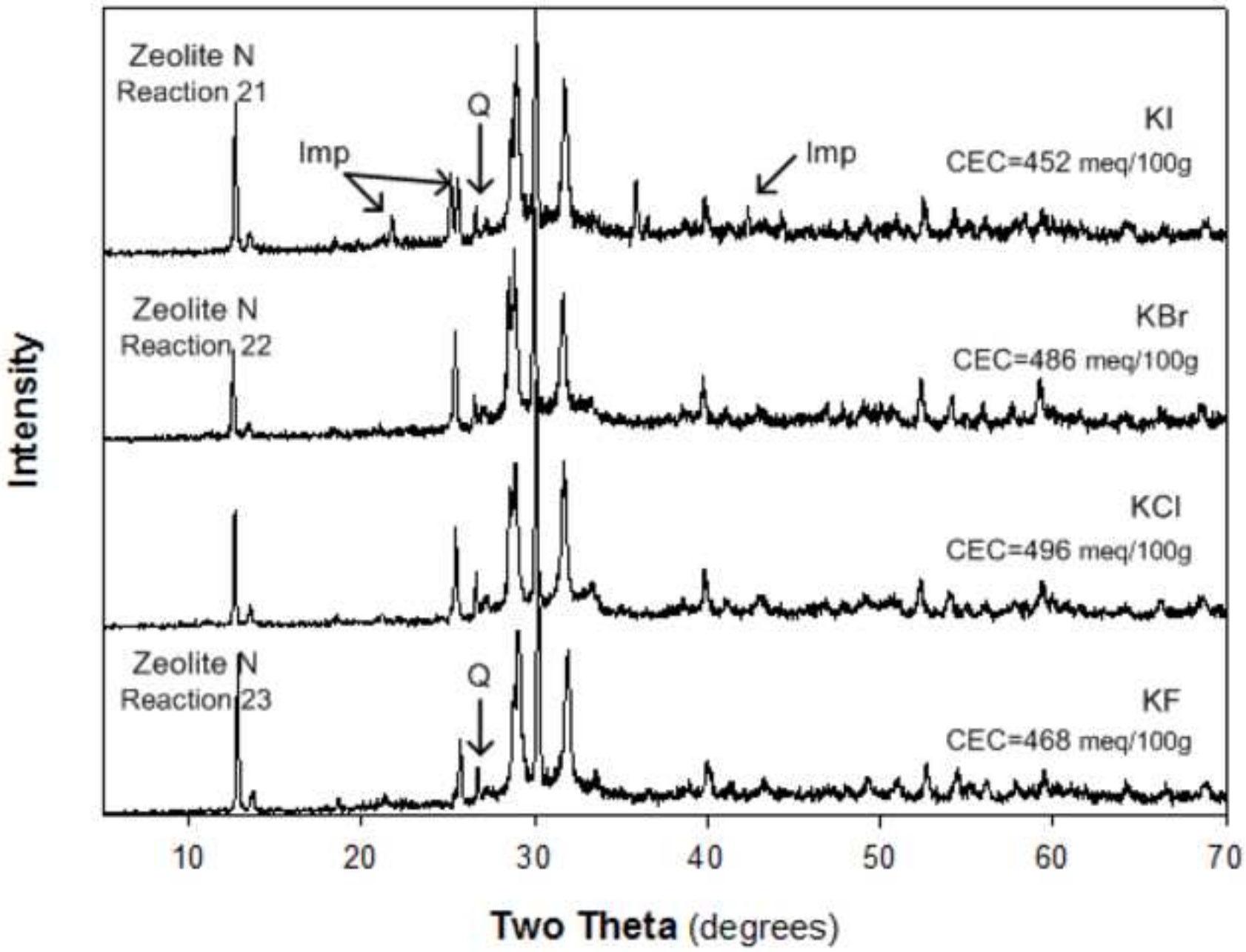

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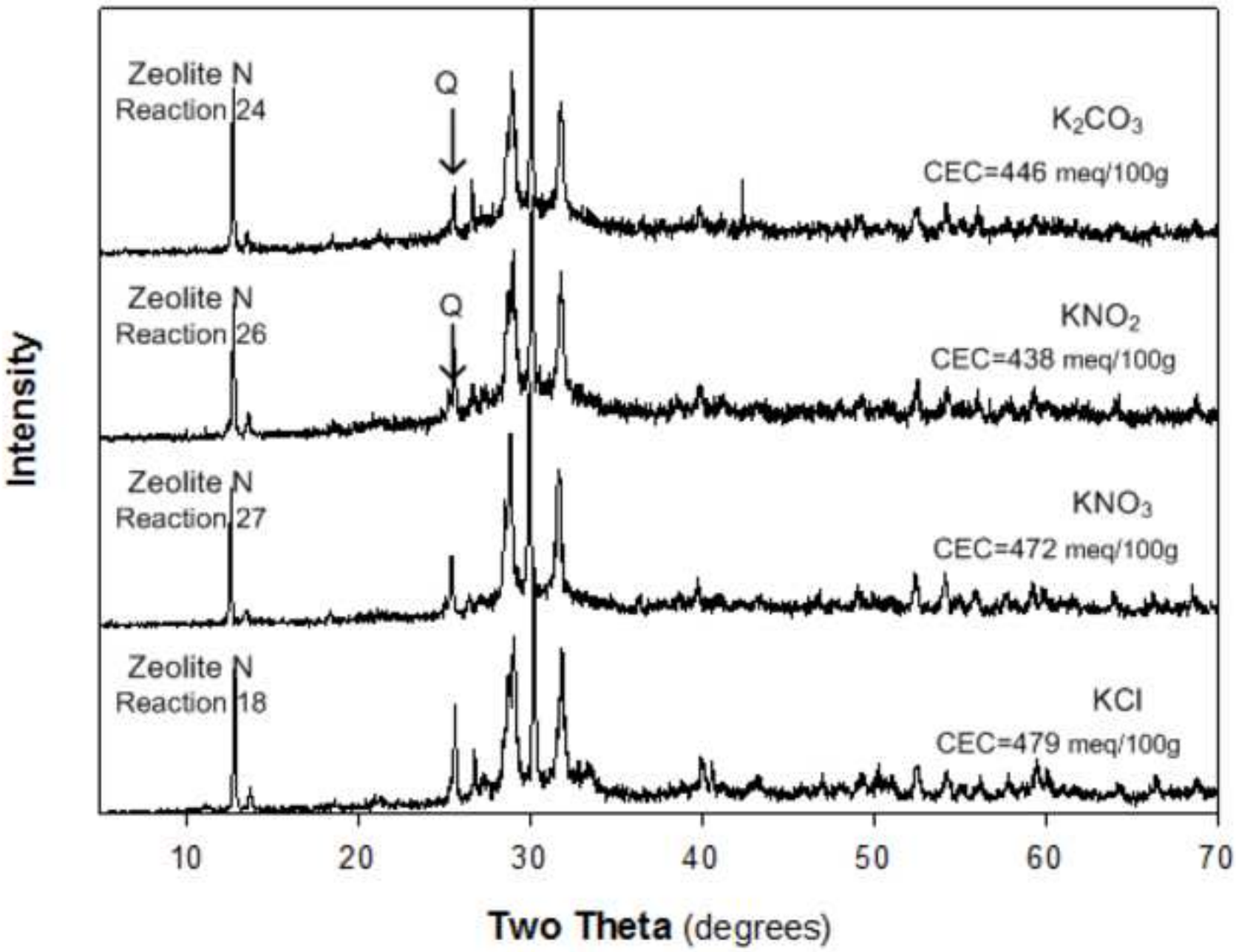

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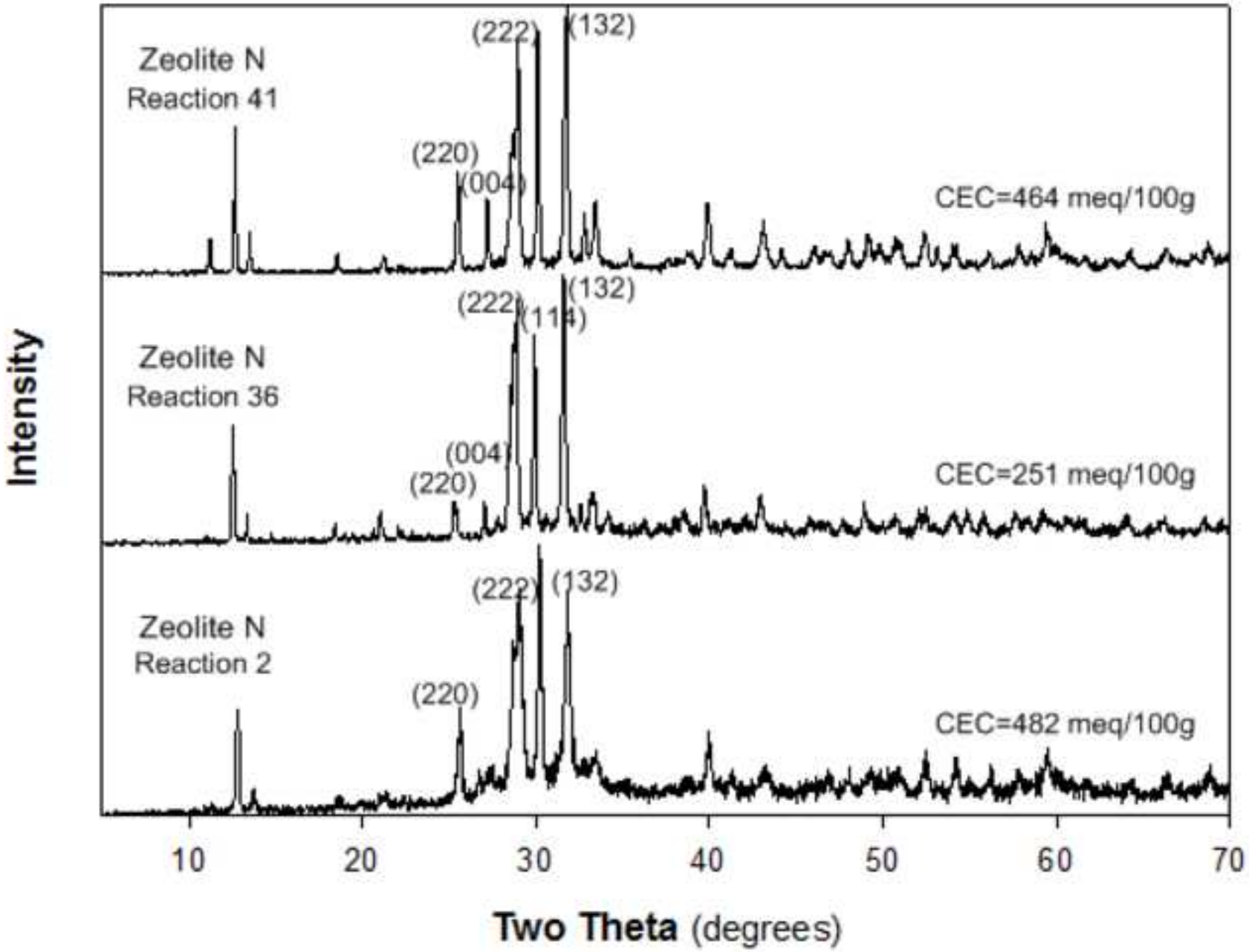

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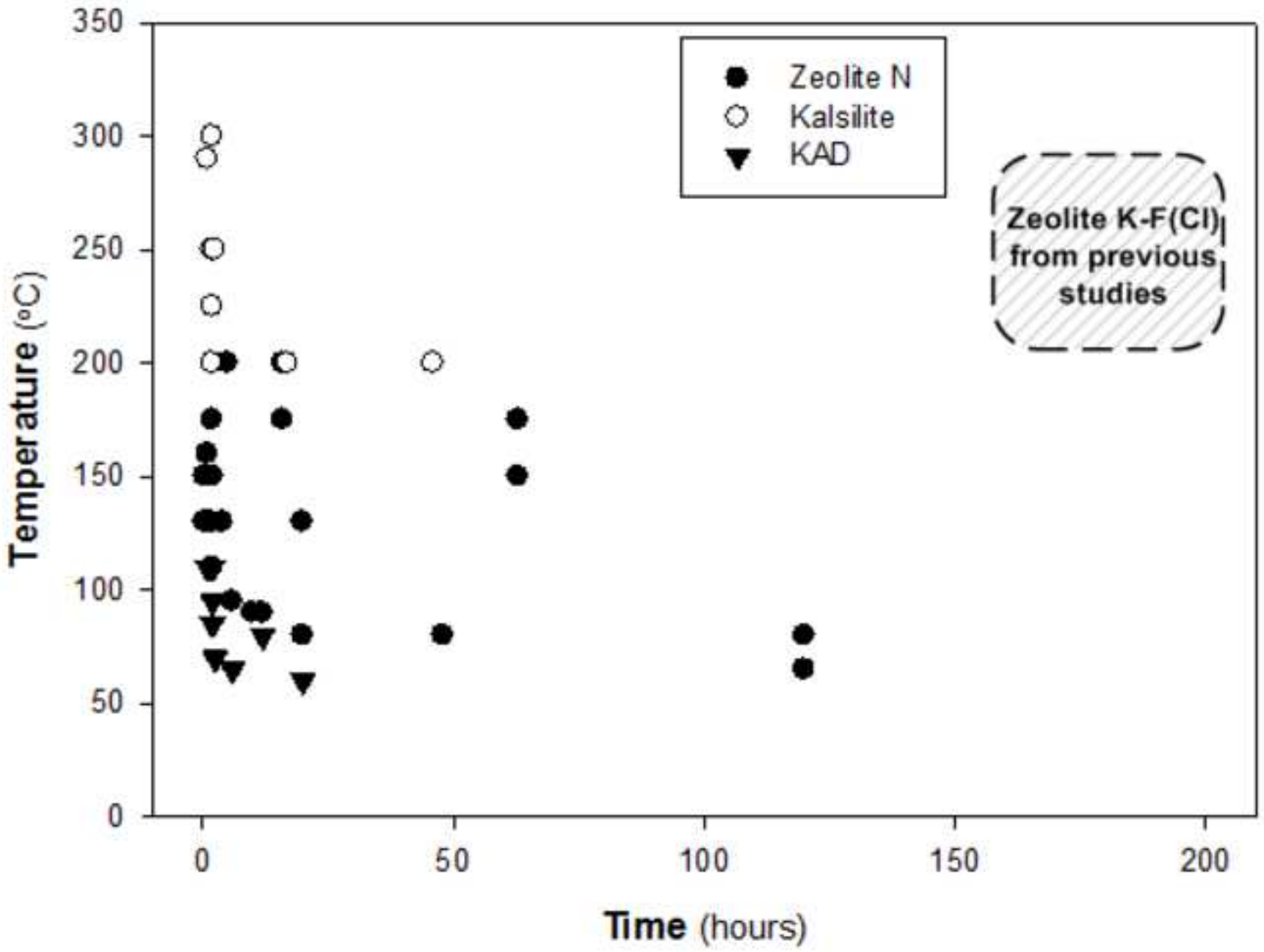

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